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Preparation of titanium mineral from vanadium titanomagnetite concentrates by hydrogen reduction and acid leaching

Zheng-pei YAN[1,2], Ying ZHANG[2], Shi-li ZHENG[2], Yang ZHANG[2],
Pei SUN[3], Zi-wei SONG[4], Faiza SAFDAR[2], Tao QI[2]

1. University of Chinese Academy of Sciences, Beijing 100049, China;
2. CAS Key Laboratory of Green Process and Engineering,
National Engineering Research Center of Green Recycling for Strategic Metal Resources,
Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China;
3. School of Materials Science and Engineering, University of Utah, Utah 84112, USA;
4. Hebei Key Laboratory of Applied Chemistry, College of Environmental and Chemical Engineering,
Yanshan University, Qinhuangdao 066004, China

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Abstract: Titanium mineral was prepared from vanadium titanomagnetite concentrates by hydrogen reduction and acid leaching. The leaching behaviors of elements like Fe, V, Mn, Al, Mg, Ca, and Si were highly related to the reduction degree. The phase compositions of the reduced materials and the leached residues were analyzed by XRD to identify the effect of reduction degree on the leaching mechanisms. The results showed that the concentrates were reduced to iron metal and titanomagnetite at 800−1000 °C for 0.5 h, and the above elements of Fe and impurities were easily leached. Deeper reduction led to the formation of ilmenite and Mg−Al spinel, which hindered leaching. Mg-bearing anosovite appeared in the further reduced materials, and the leaching rates of impurities became much lower. An upgraded titanium mineral with a normalized TiO_2 grade of 70.3% was achieved by H_2 reduction at 850 °C for 0.5 h and acid leaching, which is a satisfactory Ti resource for the preparation of titanium oxide by sulfate process.

Key words: vanadium titanomagnetite; titanium mineral; hydrogen reduction; acid leaching; phase change

1 Introduction

Titanium dioxide (TiO_2) is widely used in paint, plastics, paper, welding-rod coatings, the manufacture of mineral fibers, and so on [1]. At present, TiO_2 is mainly extracted from the ilmenite concentrates and natural rutile [2]. The development of new technologies to extract TiO_2 from unconventional minerals has great potential to open up more resources [1]. Vanadium titanomagnetites (VTM) are found throughout the world with huge reserves [3]. The TiO_2 grade in the VTM concentrates is varied with the deposits, from 1 wt.% [3] to as high as around 20 wt.% [4]. The low TiO_2 grade and the complex mineralogy pose huge difficulties in the extraction of titanium from the VTM concentrates. It is commonly considered that the recovery of TiO_2 from titanomagnetites is impossible or uneconomic in the industries.

At present, the methods treating the VTM concentrates mainly include the blast furnace (BF) process [5], the reduction and melting separation process [6], the reduction and magnetic separation process [7], and the sodium roasting and leaching process [8], and so on. Those methods mainly focus

Corresponding author: Ying ZHANG, Tel: +86-10-82544856, E-mail: zhangying@ipe.ac.cn;
Shi-li ZHENG, Tel: +86-10-82544856, E-mail: slzheng@ipe.ac.cn
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on the separation of V and Fe, while TiO_2 in the concentrates is always discarded. The recovery of TiO_2 from the VTM concentrates has still been impossible in the factories so far.

Direct preparation of TiO_2 from VTM concentrates has been investigated in recent decades. SOLE [9] proposed a leaching and solvent extraction method. The species of interest were adequately dissolved by sulfuric acid first, and then titanium and vanadium were selectively extracted by solvent extraction method from the leachate. SMOROKOV et al [10] found that most elements in the VTM concentrates could be dissolved in the ammonium fluoride (NH_4F) and hydrofluoric (HF) acid solution, and then titanium can be selectively precipitated by tuning the pH of the leachate [11]. These methods which are based on the dissolution of titanium generally require a large amount of leaching agent. OGASAWARA and ARAÚJO [12] proposed that pre-reduction is a key step for the preparation of synthetic rutile from ilmenite, notably improving the leaching kinetics of iron. It was demonstrated that iron was effectively dissolved by acid from the ilmenite after pre-reduction, while Si and Al remained in the solid residues. The combination of partial reduction by carbon and mild acid leaching has also been proposed by the authors of this paper recently, and TiO_2-enriched material could be obtained [13]. It was found that the leaching of Fe and other elements including Al, Mg, Mn, etc, was efficient and Ti could be satisfactorily enriched in the leaching residues under optimized conditions. Either deeper or lower degree of reduction was against the separation of Ti with other elements by leaching. We also confirmed that the optimally reduced phases for leaching were the mixture of $Fe_{2.5}Ti_{0.5}O_4$ and FeO; however, the internal reason is still to be uncovered.

Recently, the goal of carbon emission peak and carbon neutrality has been the hot topic covering many fields all over the world. Thus, the use of hydrogen as the reductant has attracted much attention for the reduction of greenhouse gas emissions, particularly in the iron metallurgy industry [14]. Compared with carbon [15] and carbon monoxide [16], hydrogen is clean. Unlike coal, the use of hydrogen will not introduce extra impurities including residual carbon into the system. What's more, reduction by hydrogen has an advantage in kinetics [17]. In this research, we replaced carbon with hydrogen during reduction and investigated the relationship between the effectiveness of upgrading titanium mineral and the reduction degree of the VTM. The results in this research will also shed light on the influence of the reduction degree on leaching mechanism.

2 Experimental

2.1 Materials

The VTM concentrates were obtained from Panzhihua region, China. The applied pretreatment and the characterization of the raw material, including sieving, phase composition, particle size distribution, chemical composition, and morphology, were the same as those in the previously published paper [13]. In this study, VTM concentrates with a narrow size range of 45−74 μm were used to avoid possible fluctuation. Concentrated sulfuric acid with a purity of 98.1 wt.% was purchased from Beijing Chemical Works, China. Deionized water purified by a Milli-Q (Millipore) system was used in all experiments. High-purity argon and hydrogen gas were purchased from Jinghui Gas Co., Ltd.

2.2 Experimental procedures

In each experiment, 20 g VTM concentrates were placed into a corundum crucible and then loaded into a tube furnace. After purging the tube with high-purity Ar for around 30 min, the flowing gas was switched to H_2 with a constant flowing rate of approximately 1 L/min. Then, the furnace was heated up to a pre-set temperature with a heating rate of 10 °C/min and held at this temperature for a duration of at least 0.5 h. After that, the samples were cooled to room temperature with the furnace under H_2 flow. The samples were weighed before and after reduction to calculate the mass changes. The reduced materials were leached by diluted sulfuric acid solution. The leaching was normally conducted at 80 °C for 4 h, in 0.2 mol/L sulfuric acid, with a liquid-to-solid ratio of 100 mL/g. Subsequently, the slurry was filtrated to separate the leachate and the leaching residue. The leaching residue was washed with deionized water and then dried at 80 °C for more than 10 h, while the leachate and the dried residue were collected for further analysis.

2.3 Analysis methods

The chemical compositions of the samples were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7300 V, Perkin Elmer). The pH values of the solutions were measured by an electronic pH meter (FE28, Mettler Toledo). The phase compositions of the materials were characterized by X-ray diffraction (XRD, PANalytical B.V., Empyrean). The reduced materials were also characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM, JSM−7001F, Jeol; EDS, INCA X-MAX, Oxford) to observe the morphologies.

3 Results and discussion

3.1 Tuning reduction degree

Hydrogen reduction is essentially a process to capture oxygen by hydrogen to form water vapor [18]. Thus, the mass loss of the material is a direct index to evaluate the reduction degree. Hydrogen reduction reaction may take place in the heating stage partially, but for simplicity, the reduction degree was considered to be determined by the holding temperature and the holding time. The holding temperature was changed from 650 to 1000 °C, while the holding time was mostly set to be 0.5 h. The holding time was further extended to 2 h at 900 °C and 6 h at 1000 °C, in order to explore the effect of the holding time on the reduction degree and find the reduction degree limit at 1000 °C.

The relationship between the mass loss and reduction temperature and holding time is shown in Fig. 1. As the temperature is elevated and the holding time is extended, the mass loss gradually increases. The mass loss of materials reduced at 900 °C for 2 h is measured to be 16.73%, lying between those reduced at 1000 °C for 0.5 h and 2 h, which implicates that temperature and holding time can be coordinated to tune the reduction degree. In our previous study, the concentrates were reduced by carbon and then leached by mild acid to enrich TiO_2 [13]. When VTM concentrates were reduced by carbon [13], the best separation of Fe and Ti by mild acid leaching was obtained with pre-reduction mass loss of 13.6%, which lies those between the conditions of (900 °C, 0.5 h) and (1000 °C, 0.5 h) by using hydrogen. This inspires us that the optimal conditions for hydrogen reduction seem to be 1000 °C and 0.5 h. Further extending the holding time after 4 h at 1000 °C, the mass loss does not rise evidently, implying that the reduction approaches the limit at this temperature.

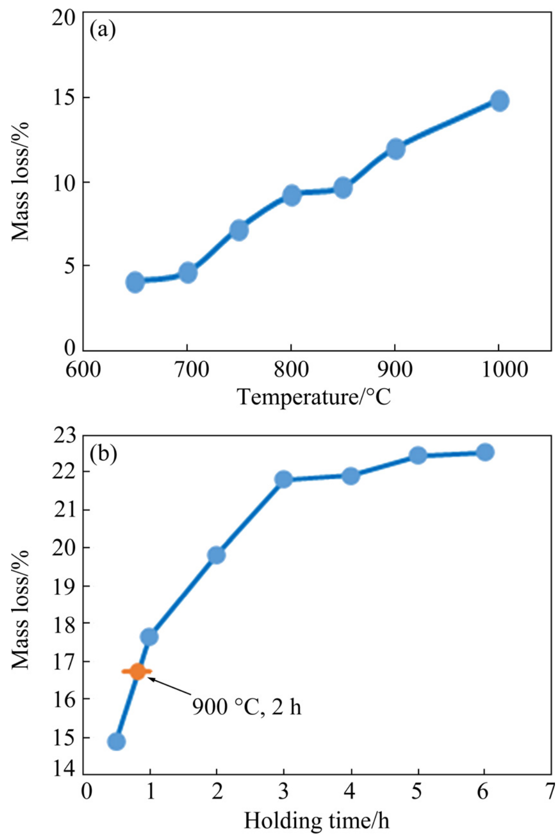

Fig. 1 Mass loss of VTM concentrates during H_2 reduction: (a) Holding for 0.5 h at various temperatures; (b) Holding at 1000 °C for various periods

3.2 Leaching behaviors of reduced VTM

The above reduced VTM was leached in 0.2 mol/L H_2SO_4 solution at 80 °C for 4 h with a liquid-to-solid ratio of 100 mL/g. The mass fraction of the leaching residue was weighed and compared in Fig. 2. It can be seen that the trend of the mass fraction of the leaching residue is not monotonously decreasing. The mass fraction reduces at a relatively fast rate with the temperature increasing from 650 to 850 °C, then the mass fraction increases slowly with the elevated temperature and reaches a peak value at 1000 °C for 1 h. Further extending the reduction time at 1000 °C, the mass fraction after leaching reduces slowly again.

Using Ti as the reference element because of its minor dissolution under the leaching conditions, the leaching rates (η) of various elements including Fe, V, Mg, Al, Mn, Ca, and Si were calculated using

Eq. (1), with the results shown in Fig. 2.

$$\eta=\frac{w_1-w_2}{w_1}\times 100\% \qquad (1)$$

where w_1 and w_2 represent the mass fraction of the researched element and titanium in the reduced material and the leached material, respectively.

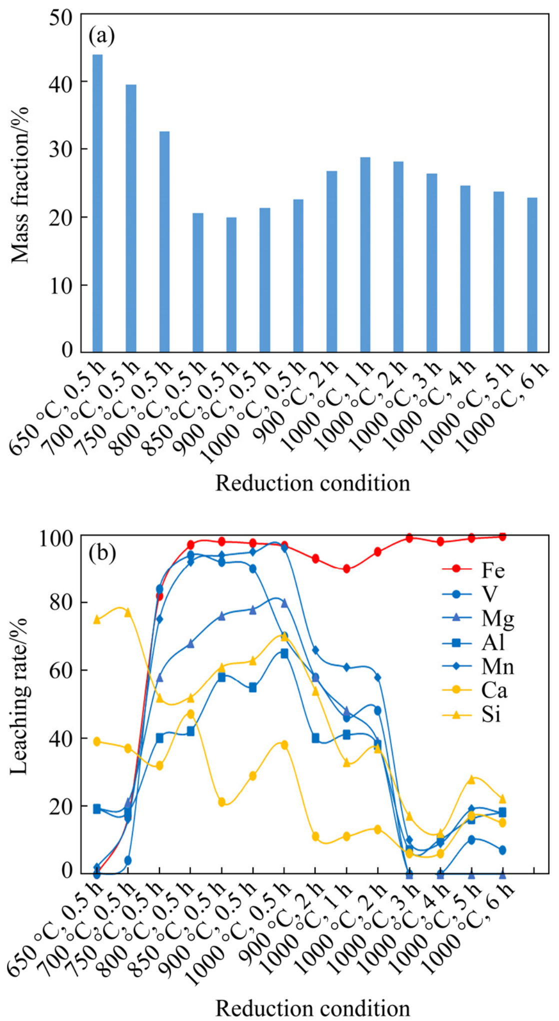

Fig. 2 Mass fractions of leaching residues and leaching rates of various elements versus reduction conditions

According to the leaching performance, the elements can be classified into three categories: Category I(Fe), Category II(V, Mg, Al, Mn), and Category III(Ca, Si). In general, the samples reduced by hydrogen at above 800 °C can ensure a Fe leaching rate of higher than 90%. The leaching rate of Fe is much higher and exceeds 97% under conditions of ((800 °C, 0.5 h); (1000 °C, 0.5 h)) and ((1000 °C, 3 h); (1000 °C, 6 h)). The leaching rates of Category II elements significantly depend on the reduction degree, displaying high values under conditions of ((850 °C, 0.5 h); (1000 °C, 0.5 h)), but low values under conditions of ((1000 °C, 3 h); (1000 °C, 6 h)). This phenomenon is of great value and indicates that the upgraded titanium minerals can be obtained by leaching reduced VTM concentrates with controlled reduction degree, which is consistent with other reports [12,13]. Besides, the leaching rates of Ca and Si generally decrease with the increase of the reduction degree.

The separation efficiency between Ti and Fe under various reduction conditions was characterized by the Fe/Ti molar ratio of the leaching residue and presented in Fig. 3. The trend is similar to that of the residue mass fraction and opposite to that of the leaching rate of Fe. This shows that the lowest Fe/Ti molar ratio, which also means the highest separation efficiency, can be obtained under the reduction parameters of ((850 °C, 0.5 h); (1000 °C, 0.5 h)) and ((1000 °C, 3 h); (1000 °C, 6 h)). However, from the perspective of making upgraded titanium minerals, the reduction parameters of ((850 °C, 0.5 h); (1000 °C, 0.5 h)) are more preferred since they also helps the separation of Ti with other impurities.

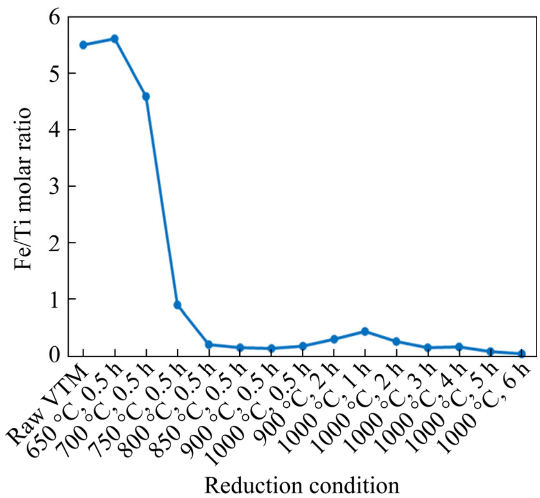

Fig. 3 Fe/Ti molar ratios of leaching residues

3.3 Leaching mechanisms of reduced materials

The phase compositions of the reduced VTM concentrates and the leaching residues were thoroughly analyzed to clarify the inherent reasons for differences in the leaching behaviors of various elements. The XRD patterns are shown in Fig. 4. The main phases for various samples were also listed in Table 1 for a clearer comparison. It can be seen from Fig. 4 and Table 1 that the phase compositions of the reduced materials are observed

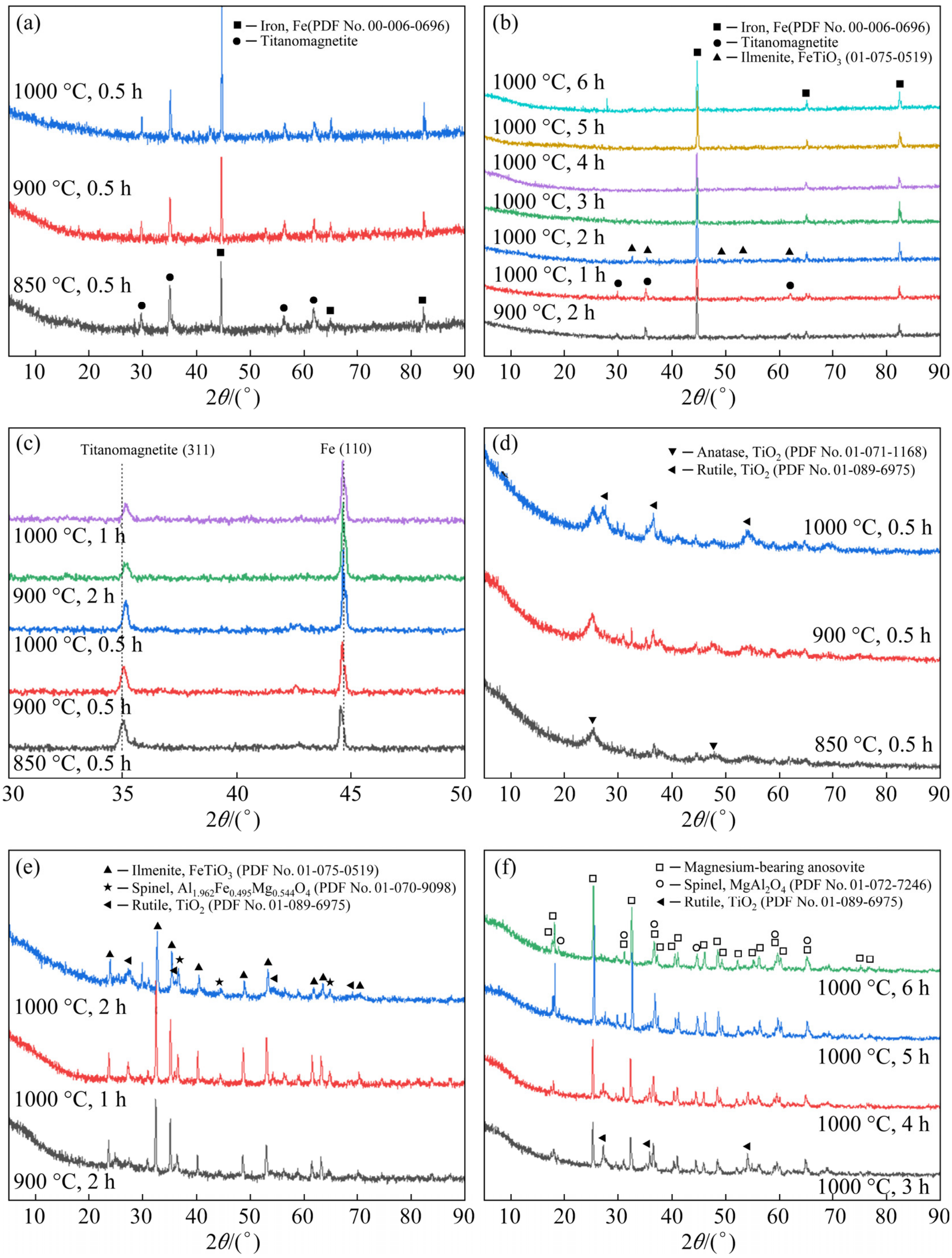

Fig. 4 XRD patterns of reduced VTM concentrates (a−c) and leaching residues (d−f) at reduction parameters

to be relatively simple, while those of the leaching residues are normally complicated. For the reduced materials, titanomagnetite and iron are the major phases with significantly stronger signals than any other phases, thus, the peaks of the minor phases in the reduced materials are too weak to be detected. Most of the major phases were removed during leaching, which helped the appearance of the minor phases in the leaching residues. Some phases such as rutile or anatase might be generated during the leaching process since the pH of the leaching solutions is changed from 1.0 to 1.5.

Firstly, the evolution of the phases during reduction is discussed. The main phases existing in the raw concentrates are Fe_3O_4 and $FeTiO_3$. In the reduced samples, titanomagnetite and iron phases are detected, while in the leaching residues, anatase, rutile, ilmenite, Mg-bearing anosovite are the major

Table 1 Phase compositions of reduced VTMs and leaching residues

Reduction condition	Composition		Reduction degree
	Reduced VTM	Leaching residue	
850 °C, 0.5 h	Fe and titanomagnetite	Anatase	Weak
900 °C, 0.5 h	Fe and titanomagnetite	Anatase	
1000 °C, 0.5 h	Fe and titanomagnetite	Anatase and rutile	
900 °C, 2 h	Fe and titanomagnetite	Ilmenite ($FeTiO_3$), spinel ($Al_{1.962}Fe_{0.495}Mg_{0.544}O_4$) and rutile	Moderate
1000 °C, 1 h	Fe and titanomagnetite		
1000 °C, 2 h	Fe and ilmenite ($FeTiO_3$)		
1000 °C, 3 h	Fe	Mg-bearing anosovite, spinel ($MgAl_2O_4$) and rutile	Deep
1000 °C, 4 h	Fe	Mg-bearing anosovite, spinel ($MgAl_2O_4$) and Rutile	
1000 °C, 5 h	Fe	Mg-bearing anosovite, spinel ($MgAl_2O_4$) and rutile	
1000 °C, 6 h	Fe	Mg-bearing anosovite and spinel ($MgAl_2O_4$)	

Ti-containing phases. Some researchers detected wustite phase [18,19] in the hydrogen-reduced VTM concentrates. However, no such phase is detected in this research, which may be because the unstable wustite phase is rapidly reduced to iron metal when it is generated [20,21]. Some researchers [18,21] have stated that TiO_2 is one of the terminal phases of the hydrogen-reduced VTMs, but the thermodynamic studies by CHEN et al [22] illustrate that the terminal phases are Ti_3O_5 and iron, with Ti_3O_5 generated by the reduction of $FeTiO_3$ and further $FeTi_2O_5$. Besides, since Mg-bearing anosovite ($Mg_nTi_{3-n}O_5$, $0\le n\le 1$) is extremely stable [23] and the crystal structures of $Mg_nTi_{3-n}O_5$, Ti_3O_5, and $FeTi_2O_5$ are similar with *Cmcm*(63) space group, Mg may replace Fe in the $FeTi_2O_5$ phase and/or replace low valence Ti in Ti_3O_5 to form $Mg_nTi_{3-n}O_5$. Thus, the possible reduction routes of VTM concentrates are as shown Reactions (2) and (3), where phases in brackets are deduced.

$$Fe_3O_4 \rightarrow (FeO) \rightarrow Fe \quad (2)$$

$$\text{Titanomagnetite} \rightarrow FeTiO_3+(FeO) \rightarrow FeTiO_3+Fe \rightarrow (FeTi_2O_5)+Fe \rightarrow Mg_nTi_{3-n}O_5+Fe \quad (3)$$

Secondly, the reduction degree-related leaching performance of Fe is naturally illustrated as follows. After the VTM is reduced at 850−1000 °C for 0.5 h, the leaching rate of Fe significantly increases compared with the as-received VTM, which is due to the ready dissolution of iron metal and ferrous iron in titanomagnetite. The leaching rate of Fe slightly decreases when further increasing the reduction degree to moderate, which is caused by the formation of ilmenite as shown in Fig. 4(e). In the deeply reduced samples, Fe in ilmenite is reduced into iron metal, and thus the leaching rate of iron increases again.

Thirdly, the reduction degree-related leaching performance of other elements is also discussed. When VTM is weakly reduced, the relatively high leaching rates of elements like Mg, Al, V, and Mn may be caused by the co-dissolution with the structure collapse of Fe-bearing phases. When the reduction degree is deepened to moderate, the Mg−Al spinel phase forms and is insoluble in dilute sulfuric acid. With further deepening the reduction degree, more spinel phases form and Mg-bearing anosovite forms also, which further lower Mg and Al dissolution. The leaching behavior of Mn and V is similar to that of Mg and Al. There are no characteristic phases of Mn and V detected in our experiments because of their much lower contents than Mg and Al contents in the as-received VTM concentrates [13]. It is possible that Mn and V do not form any characteristic phases. Instead, they are embedded in the crystal lattices of the spinel phase and the Mg-bearing anosovite phase, and thus show similar leaching performance.

To sum up, the reduction degree can be classified into three categories, weak, moderate, and deep, by using the phases of the leaching residue as the watershed. In the weakly reduced VTMs, iron and titanomagnetite are the main phases, and the leaching rates of Fe, Al, Mg, V, and Mn are relatively high. After moderate reduction, ilmenite and spinel appear, which lead to the decrease of the leaching rates of the elements in these phases. Almost all iron is reduced to iron metal in the deeply reduced VTMs, which facilitates the leaching of Fe, but the stable phases of spinel and Mg-bearing anosovite inhibit the leaching of Mg, Al, Mn, and V.

3.4 Morphologies of reduced VTMs

The morphologies of the reduced VTMs with various reduction degrees are shown in Fig. 5 and Fig. 6, which were photographed in the back-scattered electron (BSE) mode and secondary electron (SE) mode, respectively. The brighter colored phase in Fig. 5 is element iron, while the

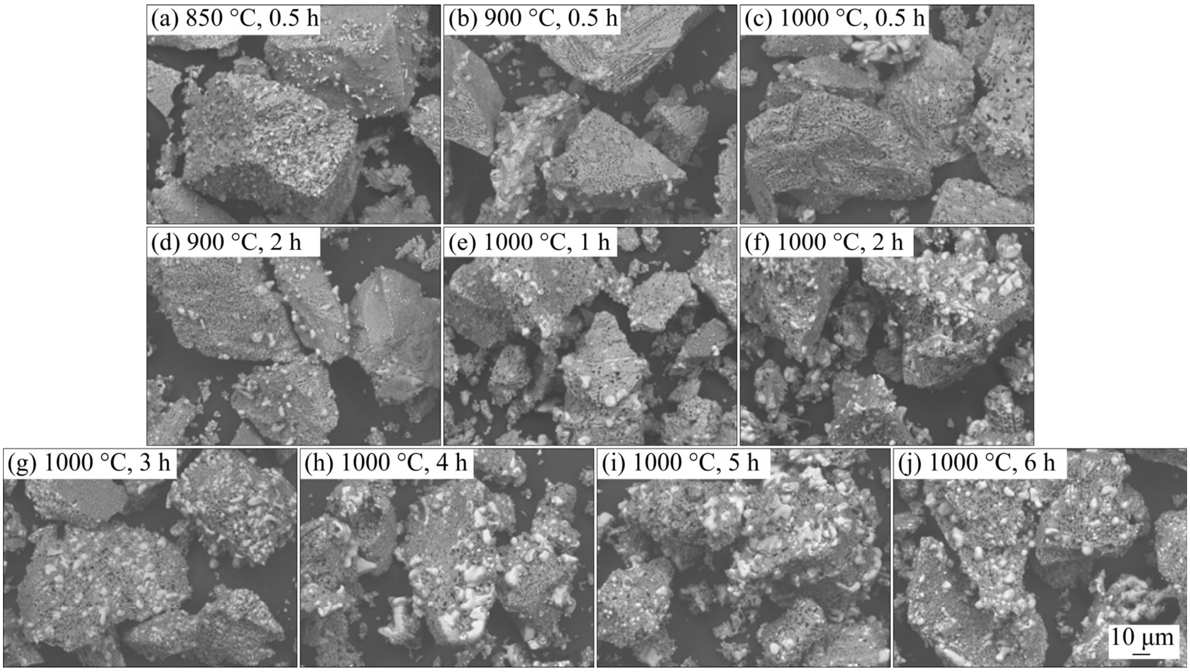

Fig. 5 Morphologies of reduced VTMs in back-scattered electron mode: (a−c) Weak reduction; (d−f) Moderate reduction; (g−j) Deep reduction

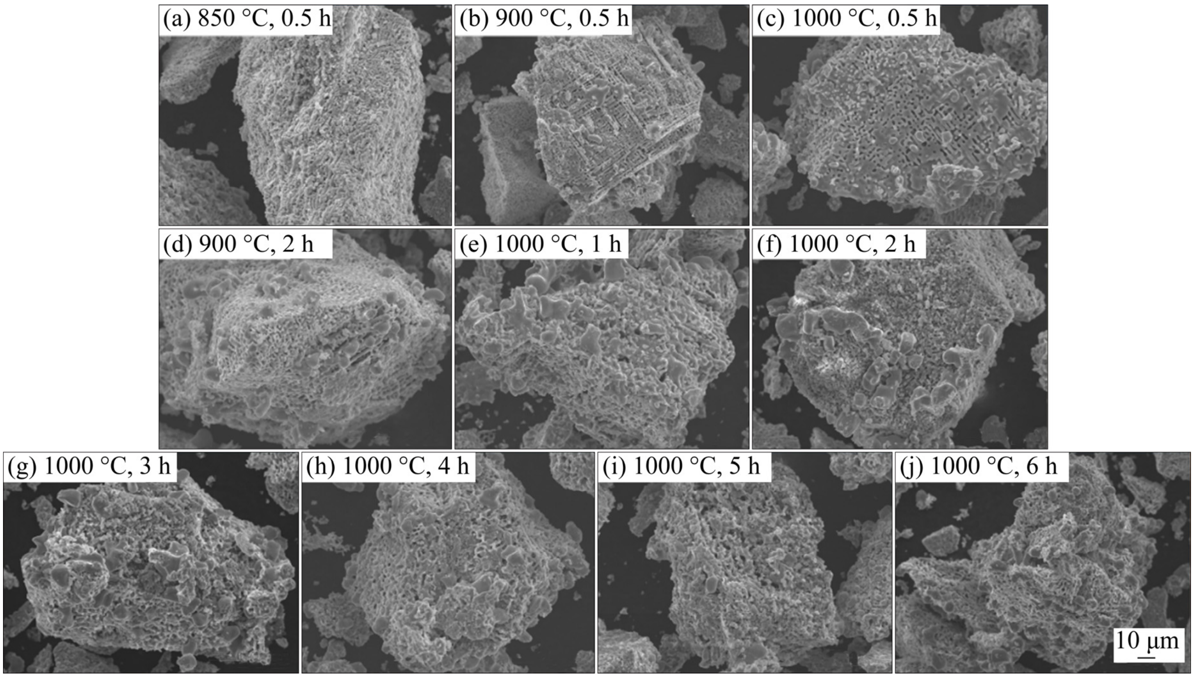

Fig. 6 Morphologies of reduced VTMs in secondary electron (SE) mode: (a−c) Weak reduction; (d−f) Moderate reduction; (g−j) Deep reduction

darker phases represent titanomagnetite and gangue phases. The phases in various areas can be roughly identified in the two figures, while Fig. 6 exhibits more detailed structural information.

The iron metal phase in a globular shape is observed in all samples in Fig. 5 and Fig. 6, which is in a needle-like shape when the VTMs are reduced by carbon under similar conditions [13]. More iron is reduced into metal at high reduction degrees, and the diffusion of the iron metal is promoted at elevated reduction temperature and extended holding time. Thus, the deeper the reduction is, the larger the size of the iron grains is.

The surface of the VTM grains with weak reduction shows grid structure, with titanomagnetite as the main phase, as shown in Figs. 7(a_1, a_2). During reduction, the Fe_3O_4 phase is reduced preferentially to form the grid structure, while the reduction of titanomagnetite is harder and slower. As the reduction degree is deepened, the grid structure disappears gradually because of the reduction of the titanomagnetite phase. Besides, sintering also promotes the disappearance of the grid structure. On the contrary, Mg, Al, and Si are detected to be enriched in the particles with a dense structure, as shown in Figs. 7(b_1, b_2).

3.5 Characterization of upgraded titanium mineral and evaluation of process

Based on the above results, weak reduction by hydrogen at 850 °C for 0.5 h should be the optimal conditions, compared to reduction by carbon at 1000 °C for 3 h with a carbon addition of 6 wt.% of VTM [13]. The corresponding leached residue was analyzed, with the normalized chemical compositions shown in Table 2. The TiO_2 content increased from 12 wt.% in the as-received VTM concentrate to more than 70 wt.% in the upgraded titanium mineral, which is a vast improvement in TiO_2 grade. Note that the TiO_2 content was diluted to around 52 wt.% by the hydrated water in the leaching residue, thus normalization was used. We could also notice that the MgO and CaO contents in the upgraded titanium mineral are still too high to be used as the Ti resources for the chloride process, because too much formation of $MgCl_2$ and $CaCl_2$ is detrimental to the chlorination reactor. Thus, this upgraded titanium mineral is more preferred as the Ti resources in the sulfate process.

Iron and vanadium are of course the other two

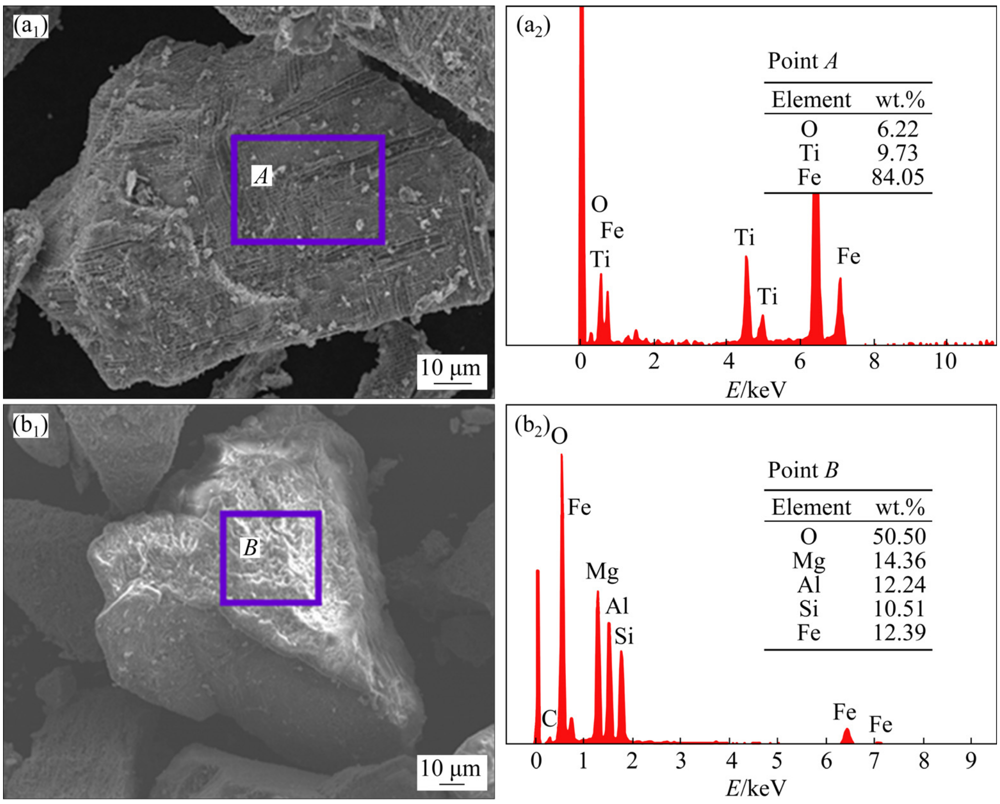

Fig. 7 SEM−EDS results of reduced VTMs at 800 °C for 0.5 h: (a_1, a_2) Weakly reduced titanomagnetite; (b_1, b_2) Particle enriched with Mg, Al and Si

important elements with concern. The leaching rates for iron and vanadium are 97.5% and 90.8%, respectively. To be clear, the concentrations of the elements in the leaching solution are shown in Table 3. Titanium was hardly detected in the leaching solution, indicating its near 100% recovery rate. Iron concentration was 6.342 g/L, vanadium concentration was 35 mg/L, and the pH value of the solution is 1.54. Even though the acidity will not bring difficulty to the precipitation of iron and vanadium, their relatively low concentrations may reduce the precipitation efficiency. But it has been demonstrated that the acid leaching conditions of 0.2 mol/L H_2SO_4 and a liquid-to-solid ratio of 100 mL/g can also be replaced at least by 0.8 mol/L H_2SO_4, and a liquid-to-solid ratio of 25 mL/g [13], indicating that there is a large room to reduce the volume of the solution and increase the elemental concentrations in the solution.

Table 2 Chemical compositions of leaching residue after calcination (wt.%)

TiO_2	Fe_2O_3	Al_2O_3	MgO	SiO_2	CaO	V_2O_5	MnO_2
70.3	9.56	8.28	3.24	5.14	3.06	0.29	0.11

Table 3 Main elemental concentrations in leaching residue with pH 1.54 (g/L)

Fe	Mg	Al	Si	Ca	V	Mn	Ti
6.342	0.144	0.124	0.088	0.013	0.035	0.029	0.005

There are also a few challenges that need to do much work. (1) One may question that subsequent leaching after reduction leads to the release of hydrogen. We measured the metallization degree after week reduction by selective leaching of Fe metal with $FeCl_3$ solution based on the reaction $2FeCl_3+Fe=3FeCl_2$, and found that 36% iron was in the metal phase. Due to the dispersed distribution and small size of the iron metal, its magnetic separation instead of leaching to avoid the generation of hydrogen is highly difficult. Whether the released hydrogen can be captured and reused or not is uncertain. (2) To find out a feasible and economic way to separate Fe and V from the acid solution and at the same time to try to regenerate the acid medium are of great importance. Beyond the strategy of iron precipitation based on the potential−pH diagram of the Fe−H_2O system, another suggested method by the authors can be used to replace H_2SO_4 with HCl for leaching and then pyro-hydrolyze the leaching solution after V precipitation to obtain high-grade Fe_2O_3 and HCl medium, which will be demonstrated in future work.

4 Conclusions

(1) The upgraded titanium mineral with normalized TiO_2 grade of 70.30 wt.% can be made from the VTM concentrate with a near 100% Ti recovery rate. The contents of CaO and MgO in the titanium mineral are still too high to be accepted by the chloride process, but this mineral can serve as the Ti resource for the sulfate process.

(2) The leaching performance of the reduced VTMs in diluted sulfuric acid was related to the reduction degree. Weak reduction performed at 800−1000 °C for 0.5 h under pure hydrogen can facilitate the separation of Ti, Fe and other impurities by leaching. Deep reduction performed at 1000 °C for 3−6 h under pure hydrogen can separate Ti and Fe, but other impurities of Al, Mg, V, and Mn cannot be separated by leaching.

(3) The leaching performance of the reduced VTMs was determined by the phase compositions. Diluted acid-dissoluble iron and titanomagnetite are the main phases in the weakly reduced VTM, while titanomagnetite is partially reduced to diluted acid-indissoluble ilmenite in the moderately reduced VTM. The formation of insoluble spinel causes a decreased leaching rate of impurities. Stubborn Mg-bearing anosovite further forms with the decomposition of the ilmenite in the deeply reduced VTM.

(4) Much work is needed to solve the challenges of hydrogen release during leaching, the utilization of iron and vanadium resources, and the regeneration of the acid medium.

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氢还原−酸浸法从钒钛磁铁精矿中制备钛富集矿物

颜正培[1,2]，张 盈[2]，郑诗礼[2]，张 洋[2]，孙 沛[3]，宋紫微[4]，Faiza SAFDAR[2]，齐 涛[2]

1. 中国科学院大学，北京 100049；
2. 中国科学院 过程工程研究所 战略金属资源绿色循环利用国家工程研究中心
中国科学院绿色过程与工程重点实验室，北京 100190；
3. School of Materials Science and Engineering, University of Utah, Utah 84112, USA；
4. 燕山大学 环境与化学工程学院 河北省应用化学重点实验室，秦皇岛 066004

摘 要：采用氢还原−酸浸法从钒钛磁铁精矿中制备钛矿物。还原料中 Fe、V、Mn、Al、Mg、Ca 和 Si 等元素的浸出行为与还原度密切相关。利用 XRD 法分析还原料与浸出渣的物相组成，确定还原度对浸出机理的影响。结果表明，在 800~1000 ℃下保温 0.5 h，精矿被还原为金属铁和钛磁铁矿相，铁和各杂质元素易浸出。深度还原使还原料中生成钛铁矿和 Mg−Al 尖晶石相，从而阻碍铁和杂质元素的浸出。更深度的还原导致含镁黑钛石的生成，显著降低杂质元素的浸出率。精矿经氢气在 850 ℃下还原 0.5 h 并酸浸后，可获得归一化 TiO_2 品位达 70.3%的钛富集矿物，是硫酸法生产钛白粉的理想原料。

关键词：钒钛磁铁矿；钛矿物；氢还原；酸浸；物相变化

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